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Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization.  
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10. Influence of Molecular Weight on the Phase Transitions of Poly( $\omega$ -[(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ether)s with Nonyl and Decanyl Alkyl Groups.

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## **ABSTRACT**

The synthesis and living cationic polymerization of 9-[(4-cyano-4'-biphenyl)oxy]nonyl vinyl ether (6-9) and 10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether (6-10) are described. The mesomorphic behavior of poly(6-9) and poly(6-10) with narrow molecular weight distributions and degrees of polymerization from 2 to 32 were discussed by comparison to that of 9-[(4-cyano-4'-biphenyl)oxy]nonyl ethyl ether (8-9) and 10-[(4-cyano-4'-biphenyl)oxy]decanyl ethyl ether (8-10) which are the model compounds of the monomeric structural units of poly(6-9) and poly(6-10). 8-9 exhibits monotropic nematic and monotropic  $s_A$  while 8-10 monotropic smectic A mesophases. Irrespective of the thermal history of the sample, over the entire range of molecular weights, poly(6-9) exhibits an enantiotropic  $s_A$  mesophase. In the first heating scan, poly(6-10) exhibits a crystalline phase followed by an enantiotropic  $s_A$  mesophase. In the second heating scan, poly(6-10)s with degrees of polymerization below 16 exhibit an enantiotropic  $s_A$  mesophase while polymers with higher degrees of polymerization display both  $s_A$  and  $s_X$  (unidentified) enantiotropic mesophases. Finally, the phase behavior of poly{ $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether}s with alkyl from ethyl to undecanyl will be discussed at four different degrees of polymerization; 30, 23, 13 and 4.

## INTRODUCTION

The dependence of phase transition temperatures on polymer molecular weight represents the most elementary relationship which should be elucidated in order to provide a systematic approach to the molecular engineering of side chain liquid crystalline polymers. The only trend which is generally accepted consists of the enlargement of the temperature range of the mesophase which occurs with the increase of the polymer molecular weight.<sup>1-15</sup> The transition from monomer to polymer can also generate the transformation of a virtual or monotropic mesophase of the monomeric structural unit or of the monomer into a monotropic or enantiotropic one. This dependence was recently explained based on thermodynamic principles assuming that the behavior of the polymer is determined by that of the monomeric structural unit.<sup>16,17</sup> However, there are several reports which have demonstrated that the number of mesophases and the nature of the mesophase are both changing by increasing the molecular weight of the polymer.<sup>4,5,7-15</sup> Although, at the first sight, this trend seems "unexpected", it was already confirmed for several different polymer systems.

Consequently, the first goal of this series of publications is to provide a complete elucidation of the influence of molecular weight on the phase behavior of poly( $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether)s containing alkyl groups from ethyl to undecanyl. We decided to investigate this particular series of polymers because their corresponding monomers can be polymerized through a living cationic polymerization mechanism and therefore, polymers with well defined molecular weights and narrow molecular weight distributions can readily become available.<sup>11-15</sup> The initiating systems which we prefer to use in these polymerizations is  $\text{CF}_3\text{SO}_3\text{H}/(\text{CH}_3)_2\text{S}$ .<sup>18</sup>

The goal of this paper is to describe the synthesis and living cationic polymerization of the last two monomers from this series, i.e., 9-[(4-cyano-4'-biphenyl)oxy]nonyl vinyl ether (6-9) and 10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether (6-10). The influence of molecular weight on their phase transitions will be discussed by comparison to that of 9-[(4-cyano-4'-biphenyl)oxy]nonyl ethyl ether (8-9) and 10-[(4-cyano-4'-biphenyl)oxy]decanyl ethyl ether (8-10) which represent the model compounds of the monomeric structural units of poly(6-9) and poly(6-10). Then, the mesomorphic behavior of poly( $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether)s with alkyl groups containing from two to eleven

methylenic units will be comparatively discussed at four different degrees of polymerization: 30, 23, 13 and 4. The implication of different phase transitions at various molecular weights on the molecular design of novel macromolecular architectures based on side chain liquid crystalline polymers is briefly discussed.

## EXPERIMENTAL

### Materials

4-Phenylphenol (98%), 1,10-phenanthroline (anhydrous, 99%), palladium (II) acetate (all from Lancaster Synthesis), ferric chloride anhydrous (98%, Fluka), copper (I) cyanide (99%), 9-borabicyclo[3.3.1]nonan (9-BBN, crystalline, 98%), 9-bromononan-1-ol (97%), 10-bromodecan-1-ol (90%) and the other reagents (all from Aldrich) were used as received. Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-BBN and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. N-Methyl-2-pyrrolidone (98%, Lancaster Synthesis) was dried by azeotropic distillation with benzene, shaken with barium oxide, filtered, and fractionally distilled under reduced pressure. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

### Techniques

$^1\text{H-NMR}$  (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks respectively. In all cases, heating and cooling rates were  $20^\circ\text{C}/\text{min}$  unless otherwise specified. Glass transition temperatures ( $T_g$ ) were read at the middle of the change in the heat capacity. For certain polymer samples, first heating scans sometimes differ from second and subsequent heating scans. At the proper place, this difference will be discussed. However, second and subsequent heating scans are identical. Although in the present case both sets of data are identical, they will be reported. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800

central processor was used to observe the thermal transitions and to analyze the anisotropic textures<sup>19,20</sup>. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin Elmer PL gel columns of 10<sup>4</sup> and 500 Å with CHCl<sub>3</sub> as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

### Synthesis of monomers

Scheme I outlines the synthesis of monomers and model compounds, while Scheme II the polymerization reaction.

#### 1,10-Phenanthroline Palladium (II) Diacetate (9)

1,10-Phenanthroline palladium (II) diacetate was synthesized according to a literature procedure.<sup>21</sup> mp, 220°C. (lit. 22, mp, 234°C).

#### 4-Cyano-4'-Hydroxybiphenyl (5)

**5** was synthesized as reported in a previous publication.<sup>11,22</sup> Purity: 99% (HPLC). mp, 195-198°C (lit. 20, 21, mp, 196-199°C). <sup>1</sup>H-NMR (acetone-d<sub>6</sub>, TMS, δ, ppm): 3.80 (1 proton, -OH, s), 7.01 (2 aromatic protons, o to -OH, d), 7.61 (2 aromatic protons, m to -OH, d), 7.70 (4 aromatic protons, o and m to-CN, s).

#### Synthesis of 4-cyano-4'-(9-hydroxynonan-1-yloxy)biphenyl (7-9)

4-Cyano-4'-hydroxybiphenyl (4.37 g, 0.0224 mol) and potassium carbonate (9.29 g, 0.067 mol) were added to a mixture of acetone-DMSO (10:1) (110 ml). 9-Bromononan-1-ol (5 g, 0.0224 mol) was added to the resulting solution which was heated to reflux for 24 hr. After cooling, the mixture was poured into water and then filtered. The obtained solid was recrystallized from methanol and then benzene, to yield 5.6 g (74.1%) of white crystals. mp, 81.4°C, T<sub>n-i</sub>, 98.9°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.01-1.95 (14 protons, -(CH<sub>2</sub>)<sub>7</sub>-, m), 3.65 (2 protons, -CH<sub>2</sub>OH, t), 4.00 (2 protons, PhOCH<sub>2</sub>-, t), 7.00 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to-CN, d of d).

#### Synthesis of 9-[(4-cyano-4'-biphenyl)oxy]nonyl vinyl ether (6-9)

4-Cyano-4'-(9-hydroxynonan-1-yloxy)biphenyl (4.0 g, 0.012 mol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.48 g, 1.2 mmol), n-butyl vinyl ether (64.6 ml) and dry chloroform (17.1 ml). The mixture was heated to 60°C for 6 hr. After cooling, it was filtered to remove the catalyst and the solvent was distilled in a rotavapor. The product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> eluent) and then recrystallized from n-hexane to yield 3.6 g (83.6%) of white crystals. Purity: 99.6% (HPLC). mp, 63.1°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.05-1.95 (16 protons, -(CH<sub>2</sub>)<sub>7</sub>-, m), 3.68 (2 protons, -CH<sub>2</sub>O-, t), 4.01 (3 protons, -OCH=CH<sub>2</sub> trans and PhOCH<sub>2</sub>-, m), 4.13 and 4.22 (1 proton, -OCH=CH<sub>2</sub> cis, d), 6.50 (1 proton, OCH=CH<sub>2</sub>, q), 7.02 (2 aromatic protons, o to alkoxy, d), 7.56 (2 aromatic protons, m to alkoxy, d), 7.69 (4 aromatic protons, o and m to-CN, d of d).

#### Synthesis of 9-[(4-cyano-4'-biphenyl)oxy]nonyl ethyl ether (8-9)

4-Cyano-4'-(9-hydroxynonan-1-yloxy)biphenyl (0.5 g, 1.48 mmol) was added to a solution containing potassium t-butoxide (0.166 g, 1.48 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (10 ml). Diethyl sulfate (0.197 ml, 1.5 mmol) was added and the reaction mixture was refluxed for 4 hr under argon. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous KOH, washed with water, dried over magnesium sulfate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub> eluent) and then was recrystallized from methanol to yield 0.32 g (59.2%) of white crystals. Purity: 99% (HPLC). mp, 75.4°C (DSC). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS, δ, ppm): 1.19 (3 protons, -OCH<sub>2</sub>CH<sub>3</sub>, t), 1.29-1.98 (14 protons, -(CH<sub>2</sub>)<sub>7</sub>-, m), 3.40 (4 protons, CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, m), 4.01 (2 protons, PhOCH<sub>2</sub>, t), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.65 (4 aromatic protons, o and m to -CN, d of d).

#### Synthesis of 4-cyano-4'-(10-hydroxydecan-1-yloxy)biphenyl (7-10)

4-Cyano-4'-hydroxybiphenyl (3.9 g, 0.02 mol), potassium hydroxide (1.12 g, 0.02 mol) and few crystals of potassium iodide were dissolved in a mixture of ethanol/water (7/3) (141.5 ml). 10-Bromodecan-1-ol (5 g, 0.21 mol) was added to the resulting solution which was heated to reflux for 24 hr. After cooling, the mixture was poured into water and then filtered. The obtained solid was recrystallized from methanol and then benzene, to yield 4.1 g (58.3%) of white



crystals. mp, 97.4°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 1.02-1.93 (16 protons,  $-(\text{CH}_2)_8-$ , m), 3.65 (2 protons,  $-\text{CH}_2\text{OH}$ , t), 4.01 (2 protons,  $\text{PhOCH}_2-$ , t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to-CN, d of d).

#### Synthesis of 10-[(4-cyano-4'-biphenyl)oxy]decanyl vinyl ether (6-10)

4-Cyano-4'-(10-hydroxydecan-1-yloxy)biphenyl (1.50 g, 4.27 mmol) was added to a mixture of 1,10-phenanthroline palladium (II) diacetate (0.17 g, 0.42 mmol), n-butyl vinyl ether (23.3 ml) and dry chloroform (18 ml). The mixture was heated to 60°C for 6 hr. After cooling, it was filtered to remove the catalyst and the solvent was distilled in a rotavapor. The product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$  eluent) and then recrystallized from n-hexane to yield 1.2 g (74.7%) of white crystals. Purity: 99.9% (HPLC). mp, 65.4°C,  $T_{\text{m}}$ , 69.8°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 1.02-1.93 (16 protons,  $-(\text{CH}_2)_8-$ , m), 3.67 (2 protons,  $-\text{CH}_2\text{O}-$ , t), 4.01 (3 protons,  $-\text{OCH}=\text{CH}_2$  trans and  $\text{PhOCH}_2-$ , m), 4.14 and 4.20 (1 proton,  $-\text{OCH}=\text{CH}_2$  cis, d), 6.49 (1 proton,  $\text{OCH}=\text{CH}_2$ , q), 7.01 (2 aromatic protons, o to alkoxy, d), 7.50 (2 aromatic protons, m to alkoxy, d), 7.65 (4 aromatic protons, o and m to-CN, d of d).

#### Synthesis of 10-[(4-cyano-4'-biphenyl)oxy]decanyl ethyl ether (8-10)

4-Cyano-4'-(10-hydroxydecan-1-yloxy)biphenyl (0.3 g, 0.85 mmol) was added to a solution containing potassium t-butoxide (0.096 g, 0.85 mmol), a catalytic amount of 18-crown-6 and dry tetrahydrofuran (10 ml). Diethyl sulfate (0.114 ml, 0.94 mmol) was added and the reaction mixture was refluxed for 4 hr under argon. After cooling, the reaction mixture was poured into chloroform. The chloroform solution was extracted with 10% aqueous KOH, washed with water, dried over magnesium sulfate and the solvent was removed in a rotavapor. The resulting product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$  eluent) and then was recrystallized from methanol to yield 0.23 g (54.2%) of white crystals. Purity: 99% (HPLC). mp, 69.1°C (DSC).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS,  $\delta$ , ppm): 1.20 (3 protons,  $-\text{OCH}_2\text{CH}_3$ , t), 1.30-1.93 (16 protons,  $-(\text{CH}_2)_8-$ , m), 3.41 (4 protons,  $\text{CH}_2\text{OCH}_2\text{CH}_3$ , m), 4.01 (2 protons,  $\text{PhOCH}_2$ , t), 7.02 (2 aromatic protons, o to alkoxy, d), 7.51 (2 aromatic protons, m to alkoxy, d), 7.66 (4 aromatic protons, o and m to -CN, d of d).

#### Cationic Polymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 hr. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to 0°C and the methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulfide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ( $[M]_0/[I]_0$ ) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. The filtered polymers were dried and precipitated from methylene chloride solutions into methanol until GPC traces showed no traces of monomer. Tables I and II summarize the polymerization results. Although polymer yields are lower than expected due to losses during the purification process, conversions were almost quantitative in all cases.

## RESULTS AND DISCUSSION

The results of the cationic polymerization of 6-9 and 6-10 are summarized in Tables I and II. The molecular weights of both poly(6-9) and poly(6-10) were controlled by varying the ratio  $[M]_0/[I]_0$ . As mentioned in the experimental part, the yields reported in Table I and II are below 100%. This is due to polymer loss resulted during the purification process. However, conversions are quantitative. Both the number average molecular weight ( $M_n$ ) and the  $M_w/M_n$  exhibit a linear dependence of  $[M]_0/[I]_0$ . The plots of these dependences are shown in Figure 1a, b and demonstrate that both monomers 6-9 and 6-10 polymerize through a living mechanism.

Table III summarizes the phase transition temperatures of 4-cyano-4'-( $\omega$ -hydroxyalkan-1-yloxy)biphenyls (7-9 and 7-10),  $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ethers (6-9 and 6-10) and of  $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl ethyl ethers (8-9 and 8-10). They were determined by a combination of DSC and thermal optical polarized microscopy techniques. The difference between the phase behavior of 7-9, 6-9 and 8-9 is determined by the functional group attached to the end of the alkyl unit. As we can observe from the data summarized in Table III, on going from 7-9 to 6-9 and to 8-9 the mesomorphic behavior of the compound changes from enantiotropic nematic to monotropic

nematic and to a combination of monotropic nematic and smectic A ( $s_A$ ). This trend is different for the same series of compounds containing a decanyl alkyl group. Thus 7-10 and 8-10 exhibit a monotropic nematic and a monotropic smectic A mesophase respectively, while 6-10 an enantiotropic nematic mesophase. Of general interest for the discussion which follows is the phase behavior of 8-9 and 8-10 which are the model compounds of the monomeric structural units of poly(6-9) and poly(6-10). In other words, 8-9 and 8-10 represent poly(6-9) and poly(6-10) with degrees of polymerization equal to one.

Heating and cooling DSC traces of poly(6-9) with degrees of polymerization from about 2.0 to 32.0 are presented in Figure 2. The heating DSC scans are identical irrespective of the thermal history of the sample. Therefore, first, second and subsequent heating scans are identical. The DSC traces obtained from the second heating and first cooling scans are exhibited in Figure 2. However, data collected from both first and second heating scans are presented in Table I and plotted in Figure 3a. The phase transition temperatures determined from the cooling scan are plotted in Figure 3b. Over the entire range of molecular weights, poly(6-9) displays only an enantiotropic  $s_A$  mesophase. This mesophase exhibits a classic focal conic fan shaped texture. As we have discussed at the beginning of this section, 8-9 displays both nematic and monotropic  $s_A$  mesophases. Since poly(6-9) with a degree of polymerization of about three shows only an enantiotropic  $s_A$  phase, it means that the slope of the  $T_{n-sA}$ - $M_n$  dependence is higher than that of the  $T_{n-i}$ - $M_n$  dependences. The intercept of these two dependences occurs below poly(6-9) reaches a degree of polymerization equal to three. A dependence like this, which however was expanding over a larger range of molecular weights was observed for both poly(6-6) and poly(6-8).<sup>12</sup> The overall behavior of poly(6-9) is of interest since this polymer does not present side chain crystallization at any molecular weight (Figure 3a, b).

The DSC traces of poly(6-10) obtained from the first and second heating and from the first cooling scans are presented in Figure 4a, b, c. Poly(6-10) presents a mesomorphic behavior which resembles that of poly(6-11).<sup>11</sup> The first and second DSC heating scans of poly(6-10) are different and therefore, both are shown in Figure 4a, b. In the first DSC heating scan, poly(6-10)s exhibit a crystalline melting followed by an enantiotropic  $s_A$  mesophase (Figure 4a). In the first cooling scan, poly(6-10)s with degree of polymerization up to sixteen exhibit the transition from

the isotropic to the  $s_A$  phase followed by a glass transition temperature (Figure 4c). Poly(6-10)s with higher degrees of polymerization exhibit the transition from the isotropic to  $s_A$  followed by a transition from the  $s_A$  to a  $s_X$  (unidentified smectic phase). On the subsequent heating (Figure 4b) and cooling (Figure 4c) scans, depending on the degree of polymerization, poly(6-10) exhibit either an enantiotropic  $s_A$  or enantiotropic  $s_A$  and  $s_X$  phases (Table II). However, if we anneal the polymer sample above the glass transition temperature after cooling and reheating, side chain crystallization occurs again and the polymer exhibits the same DSC heating scan as the first heating scan (Figure 4a).

The thermal behavior of poly(6-10) is very similar to that of poly(6-11).<sup>11</sup> The dependence of molecular weight of the mesomorphic behavior of poly(6-10) is plotted in Figure 5a for the first heating scan, in Figure 5b for the second and subsequent heating scans and in Figure 5c for the first and subsequent cooling scans.

Let us now compare the phase behavior of poly(6- $n$ ) with  $n=2$  to 11 at four different degrees of polymerization: 30, 23, 13 and 4. Figure 6a-d presents the thermal transition temperatures determined from the second heating scan, while Figure 7a-d presents the same thermal transition temperatures determined from the first heating scan. Thermal transition temperatures of poly(6-9) and poly(6-10) were determined in this paper. The results of poly(6-2), poly(6-3) and poly(6-4)<sup>14</sup>, poly(6-5) and poly(6-7),<sup>15</sup> poly(6-6) and poly(6-8)<sup>12</sup>, and poly(6-11)<sup>11</sup> were reported in previous publications from this series.

Figure 6a and b presents the thermal transitions, determined from second heating scans of poly(6- $n$ ), with degrees of polymerization of 30 and 23. Both plots demonstrate the same trend. Glass transition temperatures of poly(6- $n$ ) decrease with the increase of the polymer spacer length. Poly(6-2) with a degree of polymerization of 30 does not exhibit any mesophase. Poly(6-3) and poly(6-4) display a nematic mesophase, while poly(6-5) a  $s_A$  and a nematic mesophase. Poly(6-6), poly(6-8), poly(6-10) and poly(6-11) exhibit  $s_X$  (an unidentified smectic mesophase) and a  $s_A$  mesophase. The isotropization transition temperature increases with the increase of the spacer length. Upon decreasing the degree of polymerization, all phase transition temperatures of poly(6- $n$ ) decreased.

For polymers with short spacers, the isotropization temperature seems to follow an odd-even effect which is opposite to that observed in the case of main chain

liquid crystalline polymers containing flexible spacers.<sup>23</sup> That is, in the case of side chain liquid crystalline polymers the highest isotropization temperature is exhibited by the polymers containing odd spacers, while in the case of main chain liquid crystalline polymers by the polymers containing even spacers.<sup>23</sup> A similar behavior was observed in the case of side chain liquid crystalline polymethacrylates based on cyanobenzoyl ester and cyanophenyl ester mesogens and various spacer lengths.<sup>24,25</sup> These data, together with those of various polymers containing 4-cyanobiphenyl and other mesogenic side groups with different spacer lengths and polymer backbones seem to indicate the same trend, and are discussed in a recent review article.<sup>1</sup>

Let us compare the phase behavior of poly(6-*n*) with degrees of polymerization 30 and 23, determined from second heating scan with that determined from the first heating scans. Data collected from first heating scans are presented in Figure 7a,b. With the exception of poly(6-2), the nature of the highest temperature mesophase of all other polymers is identical, regardless of the scan it was collected from. In the first heating scan, poly(6-2) exhibits a *sx* mesophase. A *sx* mesophase is also observed in the first heating scan of poly(6-3) and poly(6-4). In the first heating scan, poly(6-10) and poly(6-11) exhibit a crystalline phase, while in their second heating scan they exhibit a *sx* phase.

Upon decreasing the degree of polymerization from 23 to 13, the phase behavior of poly(6-4) changes even more (Figure 6b and c). On the second heating scan, the highest temperature mesophases of poly(6-*n*)s with degree of polymerization 13 are identical to those of the corresponding polymers with degree of polymerization 23. However, with the exception of poly(6-5), no second mesophase is observed in the case of polymers with degree of polymerization of 13 (see Figure 6c versus b). In the first heating scan, a mesophase or crystalline phase is observed for the polymers with degrees of polymerization 13 (Figure 7c and 6c). Poly(6-*n*) with degrees of polymerization of 4 exhibit an even more drastic change of their phase behavior, particularly in the case of polymers with short flexible spacers. Thus, in the second heating scan, poly(6-2) with a degree of polymerization of 4 exhibits a nematic phase, while in the first heating scan it exhibits a *sx* and a nematic phase. Poly(6-3), poly(6-4), poly(6-5) and poly(6-6) display a nematic phase both in the second and first heating scans (Figure 6d and 7d). Both in the second and first heating scans, poly(6-6) with degree of

polymerization 4 shows a  $S_A$  and a nematic phase which overlaps each other. The main difference between the first and second heating scans of the polymers with degrees of polymerization 4 is observed for polymers poly(6-2), poly(6-3), poly(6-10) and poly(6-11) which, in addition to the phases exhibited in the second heating scan (Figure 6d), in the first heating scan present a  $S_X$  phase in the case of the first two polymers, and a crystalline phase in the case of the last two polymers (Figure 7d).

The data reported in this series of publications on the influence of molecular weight on the phase behavior of poly( $\omega$ -[(4-cyano-4'-biphenyl)oxy]alkyl vinyl ether)s provide the most comprehensive collection of results available to date on a polymer homologues series of side chain liquid crystalline polymers. They are important since they can be used to tailor make novel macromolecular architectures based on side chain liquid crystalline polymers, as well as to provide a theoretical explanation for the trends obtained from these experiments. The first series of experiments on statistical binary copolymers with well defined composition, molecular weight and molecular weight distribution, prepared by living carbocationic copolymerization have already been reported.<sup>26,27</sup> By analogy with the case of main chain liquid crystalline copolymers,<sup>23,28,29</sup> it has been demonstrated that the isomorphism of the structural units of the copolymer are determining the mesomorphic behavior of side chain liquid crystalline copolymers.<sup>26,27</sup> Since the phase behavior of poly(6-n)s is molecular weight dependent, the mesomorphic behavior of statistical copolymers based on various pairs of 6-n is also molecular weight dependent. Experiments on the molecular engineering of both statistical and sequential copolymers are in progress and will be reported in due time.

#### ACKNOWLEDGMENTS

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## FIGURE AND SCHEME CAPTIONS

Scheme 1: Synthesis of 9-[(4-cyano-4'-biphenyl)oxy]nonyl vinyl ether (6-9) and 7-[(4-cyano-4'-biphenyl)oxy]heptyl vinyl ether (6-10) and model compounds (8-9) and (8-10).

Scheme 2: Cationic polymerization of 6-9 and 6-10.

Figure 1: The dependence of the number average molecular weight ( $M_n$ ) and of the polydispersity ( $M_w/M_n$ ) of poly(6-9) (a) and poly(6-10) (b) on the  $[M]_0/[I]_0$  ratio.

Figure 2: DSC traces displayed during the second heating scan (a) and first cooling scan (b) by poly(6-9) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 3: The dependence of phase transition temperatures on the degree of polymerization of poly(6-9). a) data from first heating (fh) and second heating scan (sh): ○- $T_g$  (fh); □- $T_{SA-i}$  (fh); ●- $T_g$  (sh); ■- $T_{SA-i}$  (sh); b) data from first cooling scan: ■- $T_{i-SA}$ ; ●- $T_g$ .

Figure 4: DSC traces displayed during the first heating scan (a), the second heating scan (b) and first cooling scan (c) by poly(6-10) with different degrees of polymerization (DP). DP is printed on the top of each DSC scan.

Figure 5: The dependence of phase transition temperatures on the degree of polymerization of poly(6-10). a) data from first heating scan: ○- $T_g$ ; ■- $T_{K-SA}$ ; □- $T_{SA-i}$ ; b) data from second heating scan: ○- $T_g$ ; ▲- $T_{SX-SA}$ ; □- $T_{SA-i}$ ; c) data from first cooling scan: ■- $T_{i-SA}$ ; ▲- $T_{SA-SX}$ ; ●- $T_g$ .

Figure 6: The dependence of phase transition temperatures on the length (n) of flexible spacer  $[-(CH_2)_n-]$  of poly(6-n) at similar degrees of polymerization.

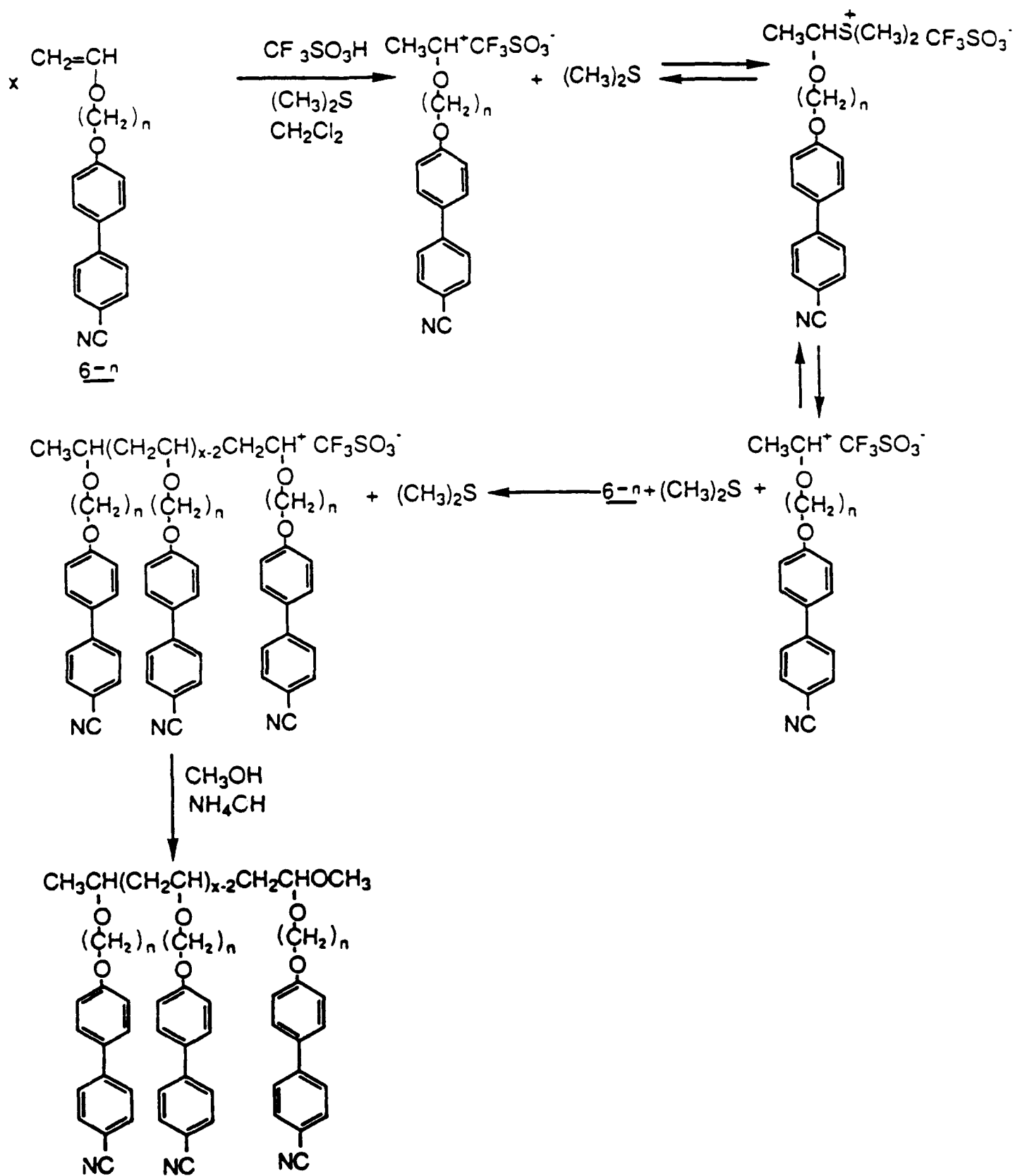
a) data from second heating scan at DP=30: O-Tg;  $\blacklozenge$ -TsX-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i; b) data from second heating scan at DP=23: O-Tg;  $\blacklozenge$ -TsX-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i; c) data from second heating scan at DP=13: O-Tg;  $\square$ -TsA-i;  $\triangle$ -Tn-i; d) data from second heating scan at DP=4: O-Tg;  $\square$ -TsA-i;  $\triangle$ -Tn-i

Figure 7: The dependence of phase transition temperatures on the length (n) of flexible  $[-(\text{CH}_2)_n-]$  spacer of poly(6-n) at similar degrees of polymerization.

a) data from first heating scan at DP=30: O-Tg;  $\blacklozenge$ -TsX.sA(n);  $\blacksquare$ -Tk-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i; b) data from first heating scan at DP=23: O-Tg;  $\blacklozenge$ -TsX.sA(n);  $\blacksquare$ -Tk-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i; c) data from first heating scan at DP=13: O-Tg;  $\blacklozenge$ -TsX.sA(n);  $\blacksquare$ -Tk-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i; d) data from first heating scan at DP=4: O-Tg;  $\blacklozenge$ -TsX-n;  $\blacksquare$ -Tk-sA;  $\square$ -TsA-i;  $\triangle$ -Tn-i.



### Scheme I



Scheme II

Table I. Cationic Polymerization of 9-[4-Cyano-4'-biphenyl]oxylnonyl Vinyl Ether (6-9) (polymerization temperature, 0°C; polymerization solvent, methylene chloride;  $[M]_0/[I]_0=0.275$ ;  $[(CH_3)_2S]/[I]_0=10$ ; polymerization time, 1hr) and Characterization of the Resulting Polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	$[M]_0/[I]_0$	Polymer yield(%)	G P C			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
			$M_n \times 10^{-3}$	Mw/Mn	D P	heating	cooling
1	2.0	44.2	0.94	1.54	2.6	g -1.6 sA 104.1 (0.70) i g -1.6 sA 103.8 (0.71) i	i 100.3 (0.71) sA -6.7 g
2	4.0	31.0	1.82	1.13	5.0	g 5.8 sA 120.6 (0.67) i g 5.0 sA 120.2 (0.70) i	i 114.7 (0.69) sA 0.8 g
3	6.0	55.9	2.03	1.24	5.6	g 11.7 sA 125.1 (0.60) i g 9.2 sA 124.4 (0.64) i	i 119.7 (0.64) sA 3.3 g
4	8.0	61.6	2.89	1.07	7.9	g 10.1 sA 131.8(0.64) i g 9.4 sA 131.9 (0.65) i	i 124.3 (0.63) sA 4.2 g
5	10.0	68.0	3.79	1.20	10.4	g 12.0 sA 135.9 (0.62) i g 11.1 sA 135.9 (0.63) i	i 130.0 (0.63) sA 5.0 g
6	13.0	63.3	4.50	1.20	12.4	g 13.3 sA 141.5 (0.62) i g 12.5 sA 141.0 (0.60) i	i 136.7 (0.61) sA 7.5 g
7	18.0	65.3	5.89	1.28	16.2	g 13.3 sA 144.7 (0.62) i g 12.7 sA 144.7 (0.62) i	i 138.7 (0.61) sA 7.5 g
8	23.0	69.3	8.35	1.16	22.9	g 13.8 sA 149.9 (0.60) i g 13.0 sA 150.7 (0.59) i	i 145.8 (0.59) sA 9.8 g
9	30.0	74.3	11.55	1.12	31.7	g 14.2 sA 153.8 (0.62) i g 14.2 sA 153.6 (0.59) i	i 149.0 (0.58) sA 10.0 g

Table II. Cationic Polymerization of 10-[4-Cyano-4'-biphenyl)oxy]decanyl Vinyl Ether (6-10) (polymerization temperature, 0°C; polymerization solvent, methylene chloride;  $[M]_0/[I]_0=0.265$ ;  $[(CH_3)_2S]_0/[I]_0=10$ ; polymerization time, 1hr) and Characterization of the Resulting Polymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	$[M]_0/[I]_0$	Polymer yield(%)	G P C			phase transitions(°C) and corresponding enthalpy changes (kcal/mru)	
			$M_n \times 10^{-3}$	Mw/Mn	D P	heating	cooling
1	4	71.3	1.40	1.15	3.7	g 3.6 k 51.1 (3.77) sA 116.6 (0.83) i g 0.0 sA 115.9 (0.86) i	i 110.9 (0.82) sA -5.5 g
2	7	66.0	2.57	1.13	6.8	g 8.7 k 49.7 (2.70) sA 128.1 (0.78) i g 2.7 sA 127.6 (0.80) i	i 122.0 (0.79) sA -0.1 g
3	10	78.0	4.23	1.08	11.2	g 11.8 k 53.4 (2.34) sA 139.5 (0.77) i g 6.4 sA 138.6 (0.76) i	i 132.4 (0.74) sA 2.7 g
4	15	74.0	6.07	1.09	16.1	g 12.7 k 53.8 (2.68) sA 147.0 (0.78) i g 14.8 sX 37.0 (0.62) sA 147.8 (0.76) i	i 142.9 (0.73) sA 24.9 (0.58) sX 9.8 g
5	20	84.7	7.29	1.14	19.3	g 15.5 k 55.0 (2.39) sA 153.7 (0.76) i g 16.2 sX 44.9 (0.68) sA 152.9 (0.74) i	i 147.3 (0.72) sA 37.4 (0.80) sX 11.8 g
6	25	82.7	9.59	1.10	25.4	g 16.2 k 55.2 (2.35) sA 155.2 (0.75) i g 16.0 sX 48.2 (0.69) sA 154.1 (0.72) i	i 149.1 (0.71) sA 41.8 (0.84) sX 12.2 g
7	30	73.3	10.91	1.09	28.9	g 17.4 k 56.1 (2.35) sA 156.5 (0.78) i g 16.5 sX 50.6 (0.91) sA 157.0 (0.71)	i 151.2 (0.70) sA 44.1 (0.84) sX 12.8 g

Table III. Thermal Characterization of 4-Cyano-4'-( $\omega$ -hydroxyalkan-1-yloxy)biphenyls (7-9) and (7-10),  $\omega$ -[(4-Cyano-4'-biphenyl)oxy]alkyl Vinyl Ethers (6-9) and (6-10), and of  $\omega$ -[(4-Cyano-4'-biphenyl)oxy]alkyl Ethyl Ethers (8-9) and (8-10).

Compound	phase transitions (°C) and corresponding enthalpy changes (kcal/mol)	
	heating	cooling
<u>7-9</u>	k 81.4 (9.10) n 98.9 (0.34) i	i 96.0 (0.35) n 54.9 (6.45) k
<u>6-9</u>	k 63.1 (10.20) i [n 59.2 (0.36) i]*	i 56.2 (0.33) n 28.9 (7.31) k
<u>8-9</u>	k 75.4 (10.22) i	i 53.2 (0.29) n 50.3 (-)* s <sub>A</sub> 41.3 (8.23)* k
<u>7-10</u>	k 97.4 (10.0) i [n 97.2 (0.45) i]*	i 94.2 (0.52) n 75.5 (8.3) k
<u>6-10</u>	k 65.4 (8.4) n 69.8 (0.36) i]	i 66.1 (0.43) n 52.6 (8.19) k
<u>8-10</u>	k 69.1 (12.9) i [s <sub>A</sub> 65.0 (0.71)]*	i 57.1 (0.72) s <sub>A</sub> 27.9 (8.66) k

\*[ ] virtual data

\* overlapped peaks

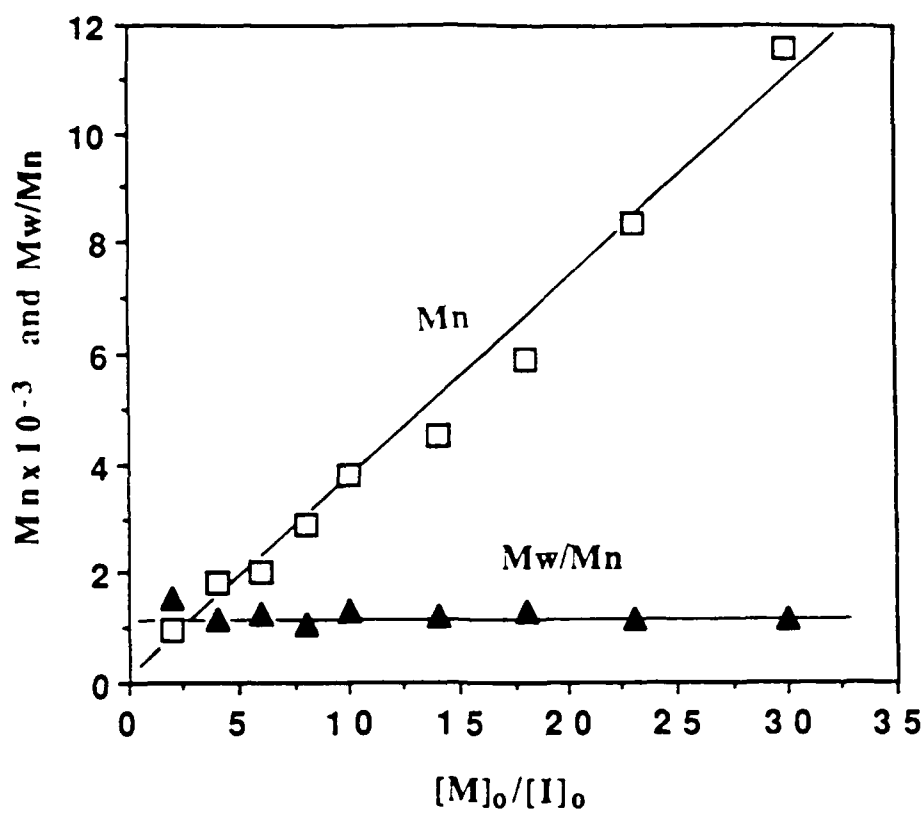


Figure 1a

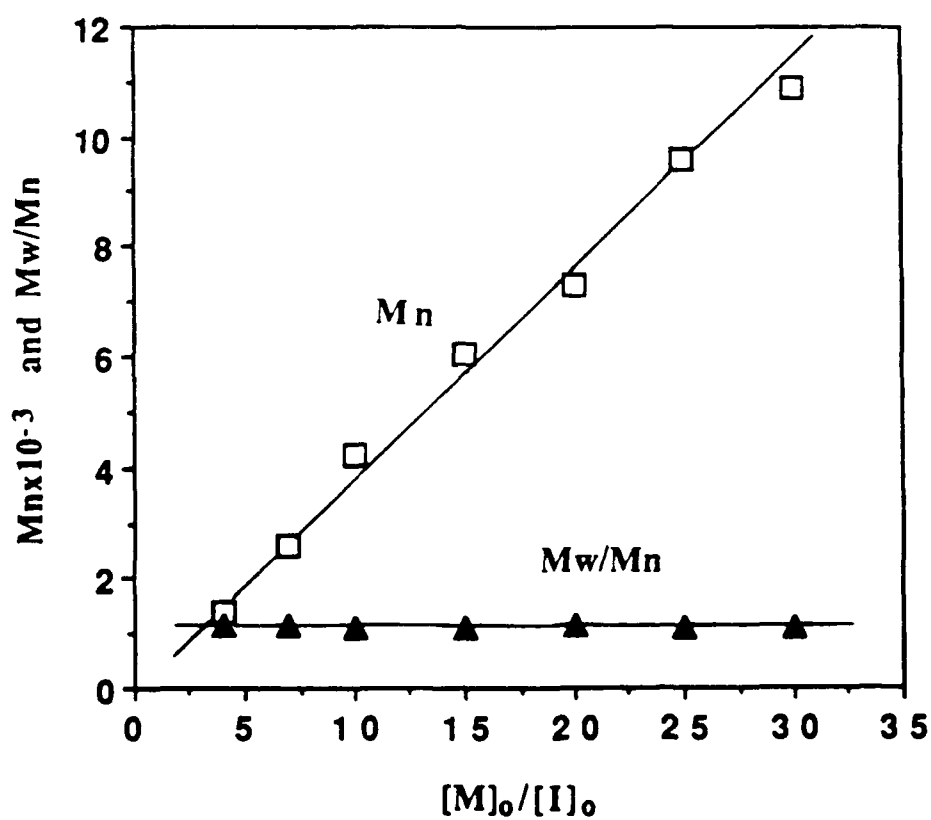


Figure 1b



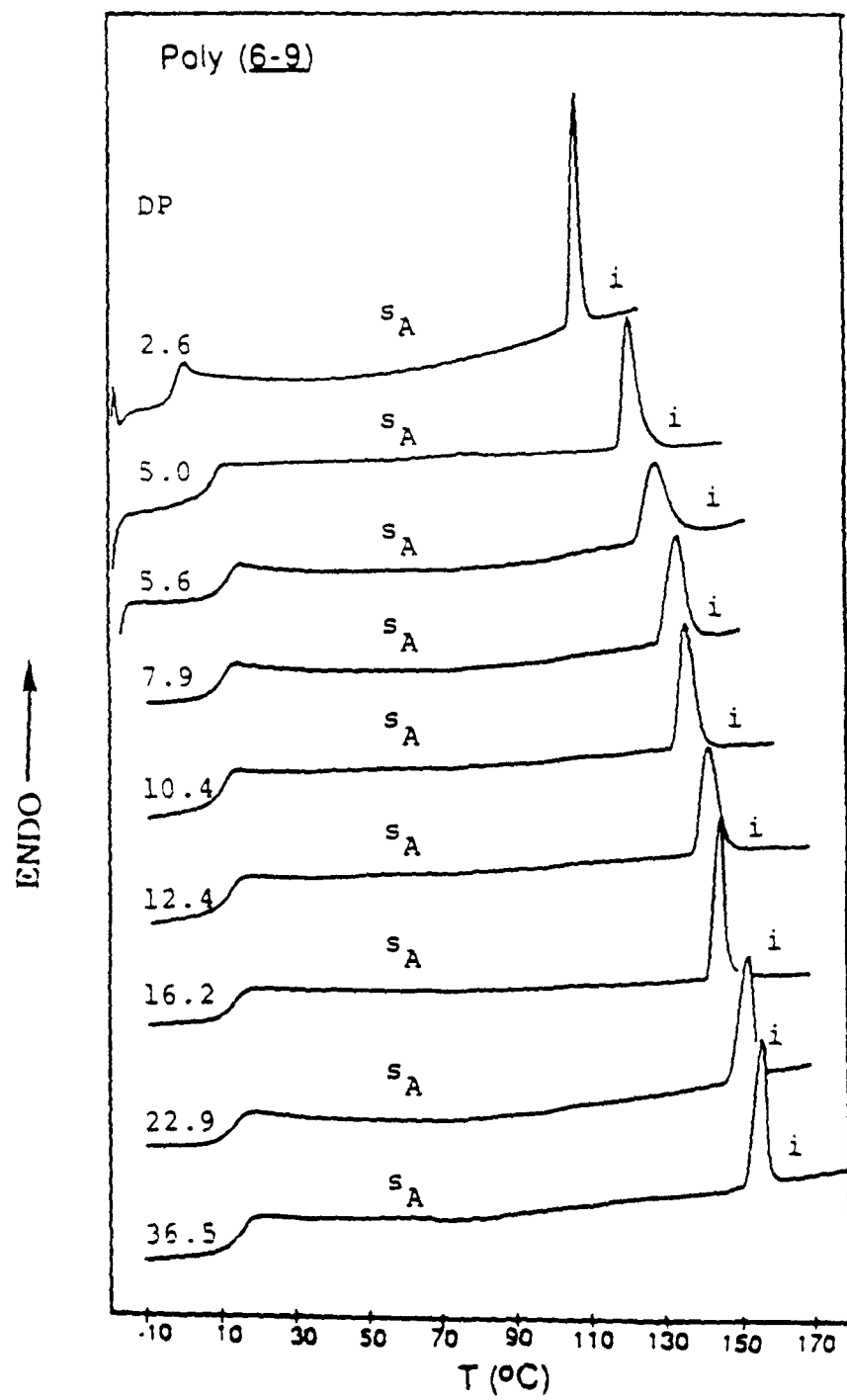


Figure 2a

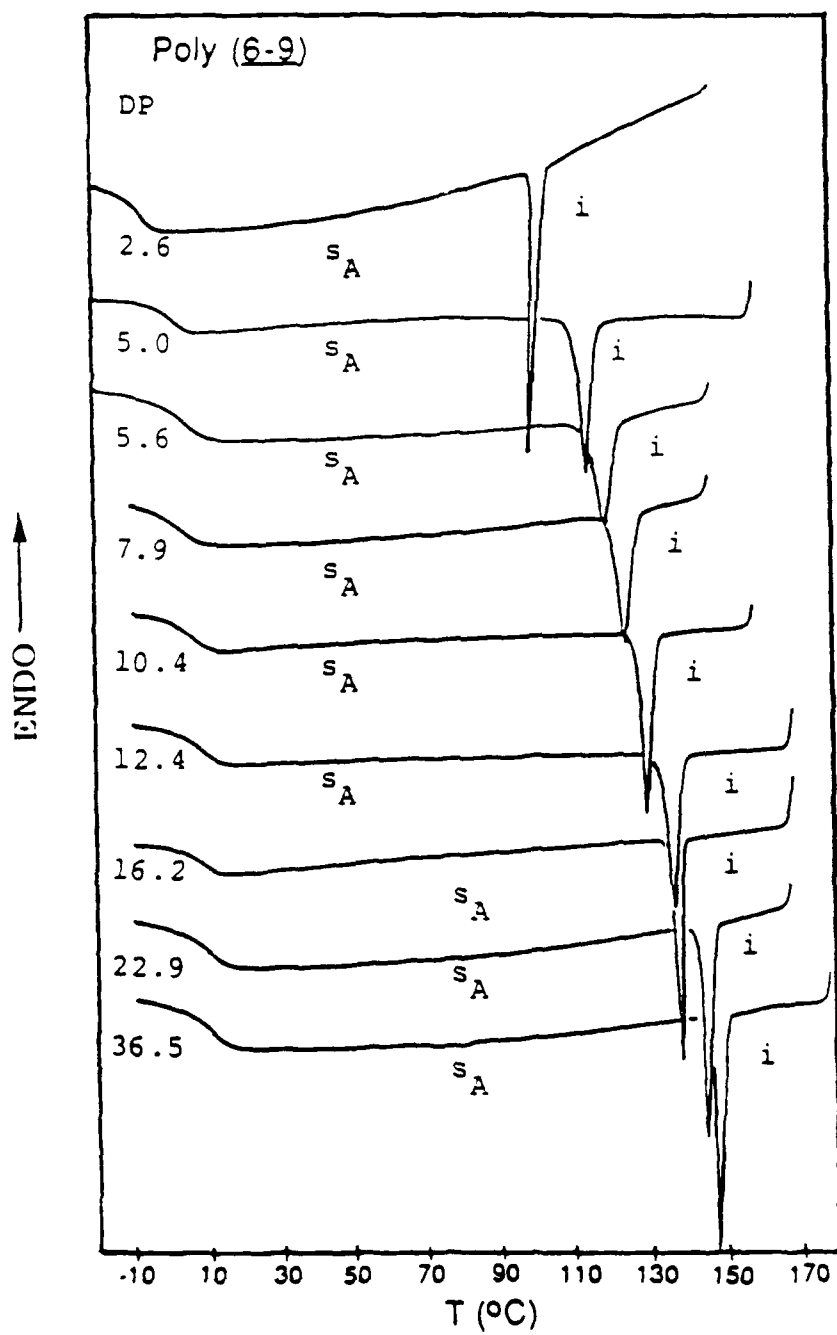


Figure 2b

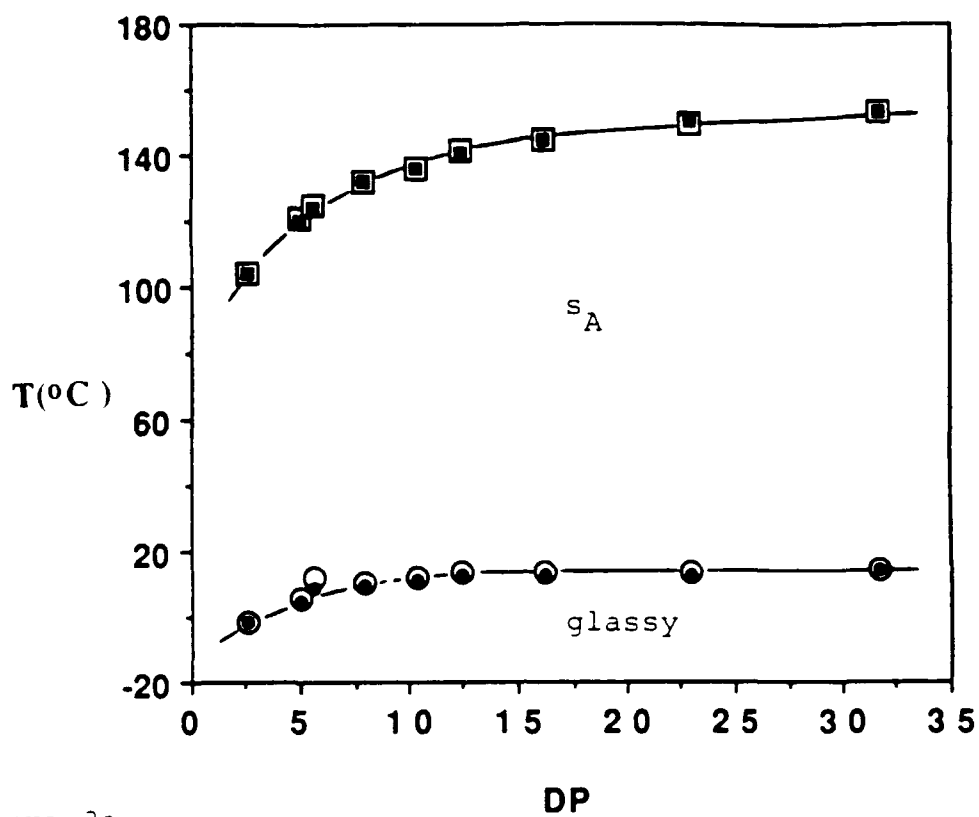


Figure 3a

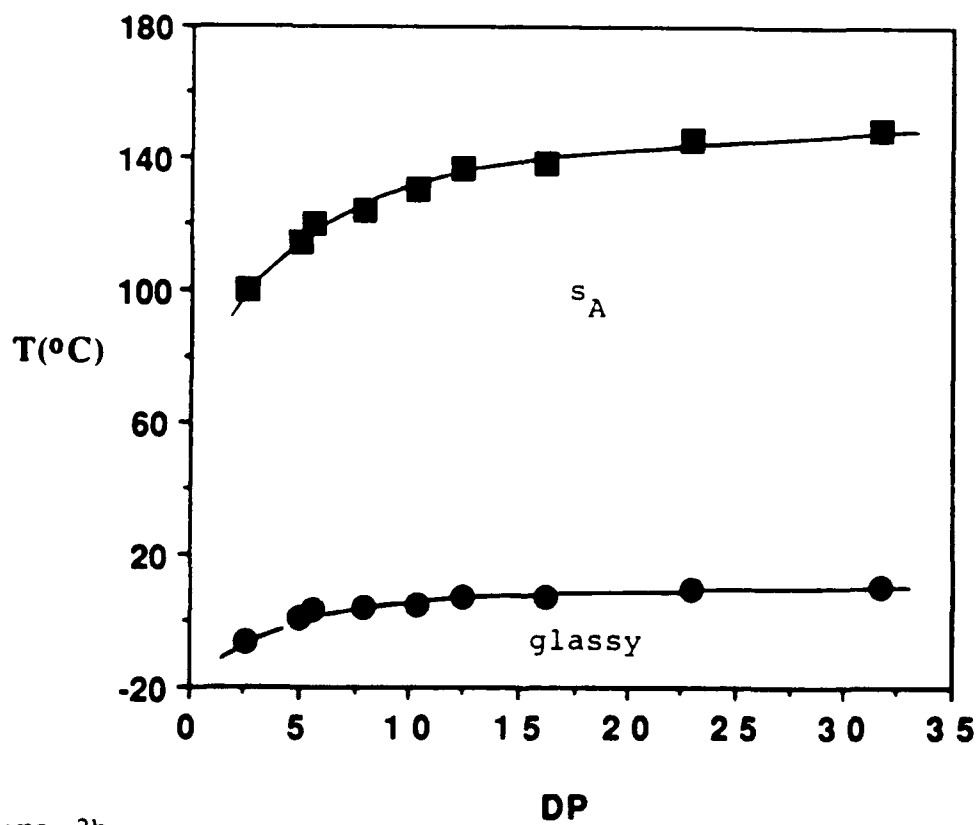


Figure 3b

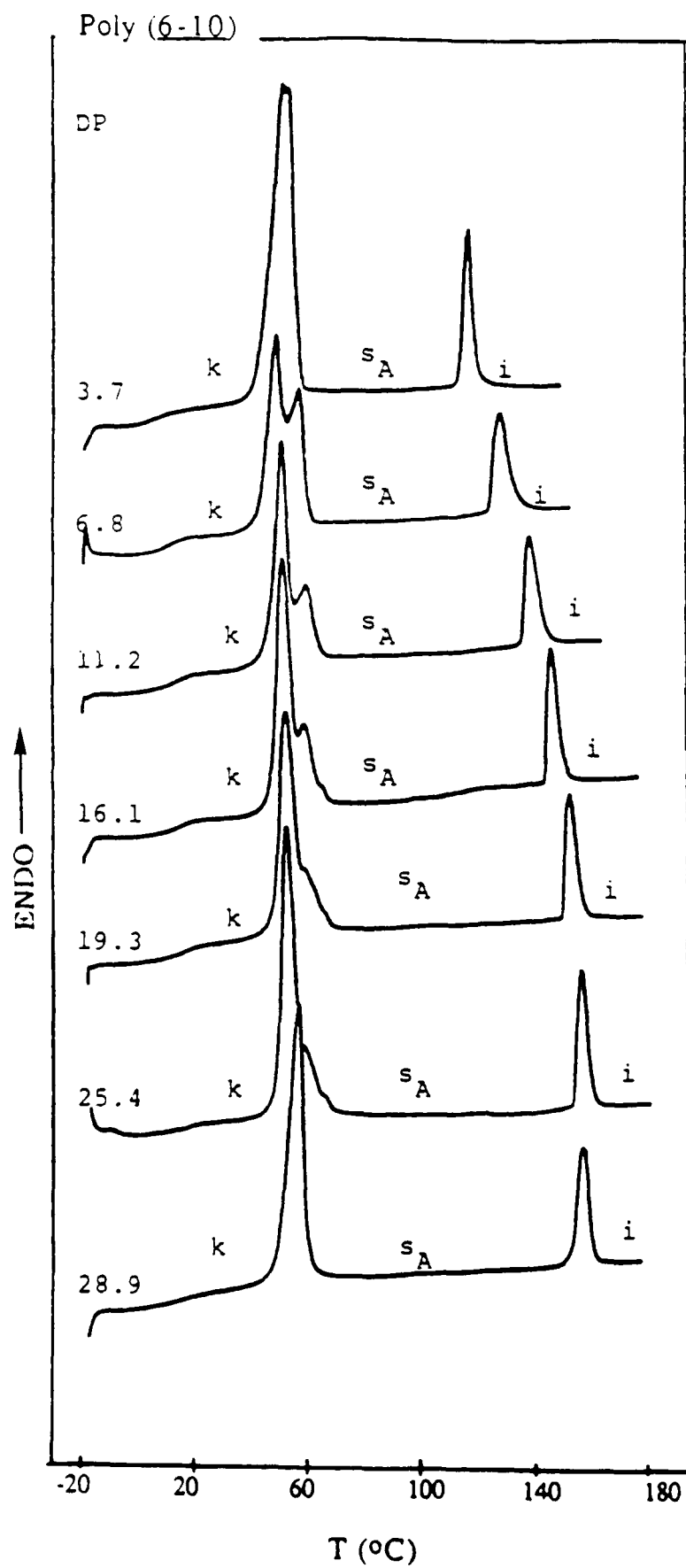


Figure 4a

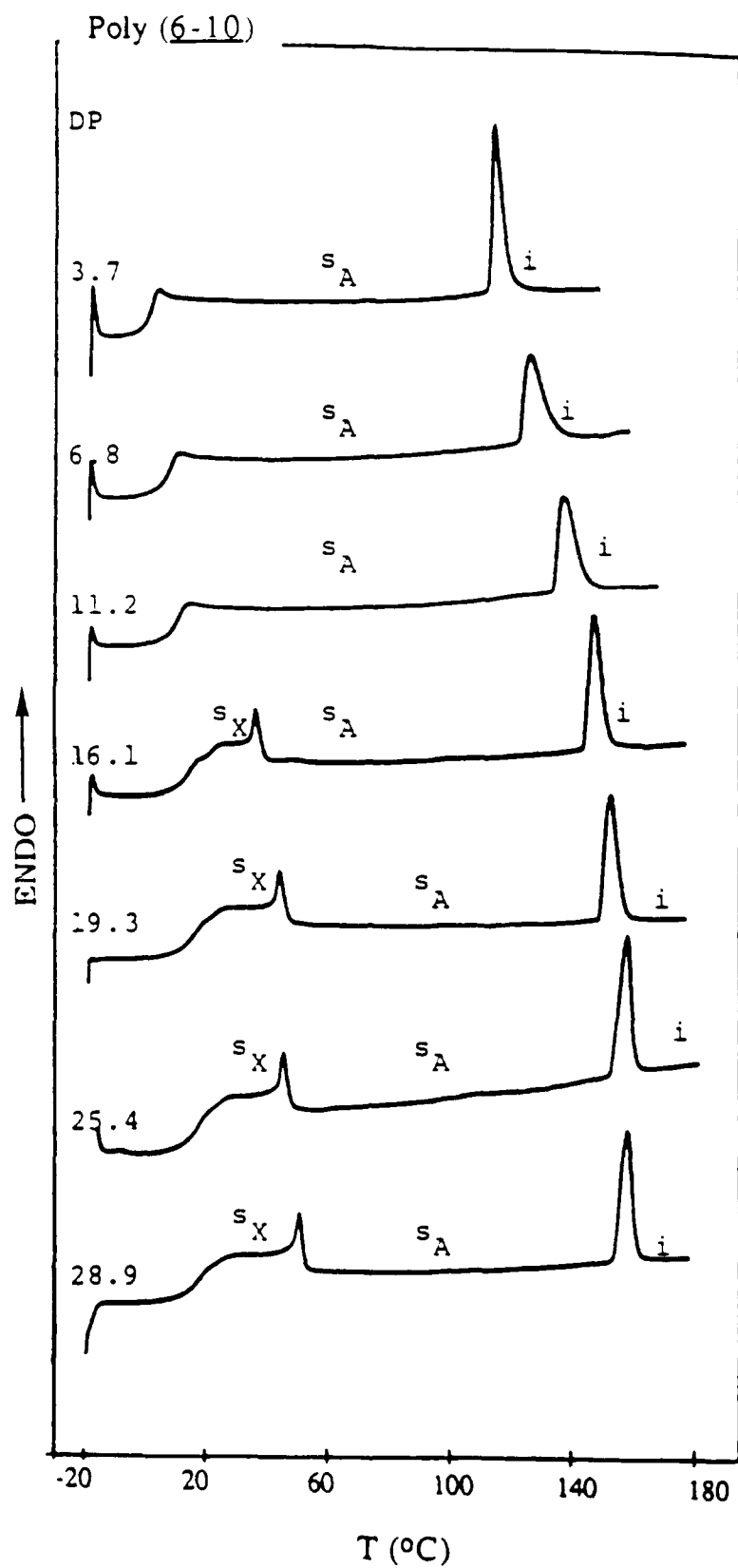


Figure 4b

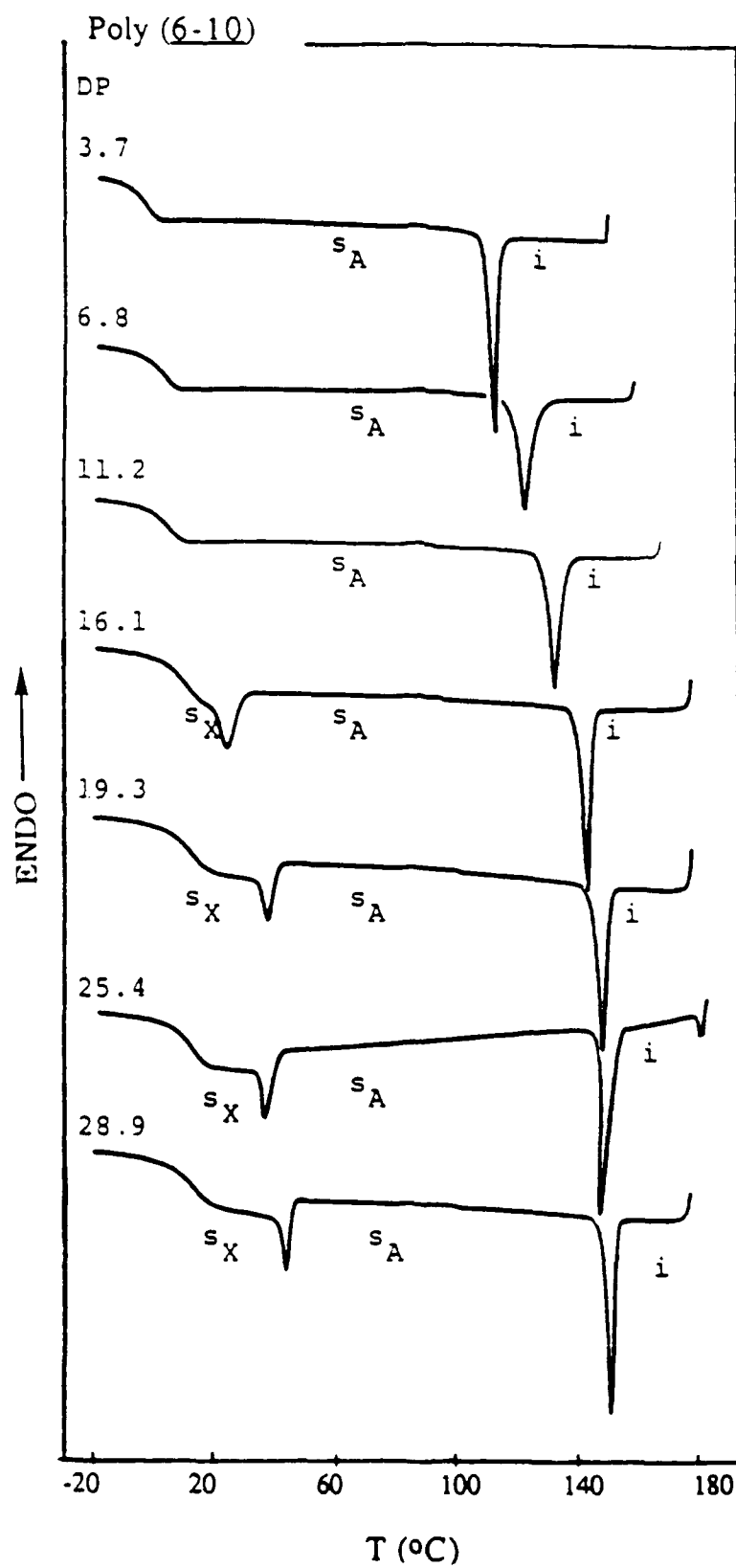


Figure 4c

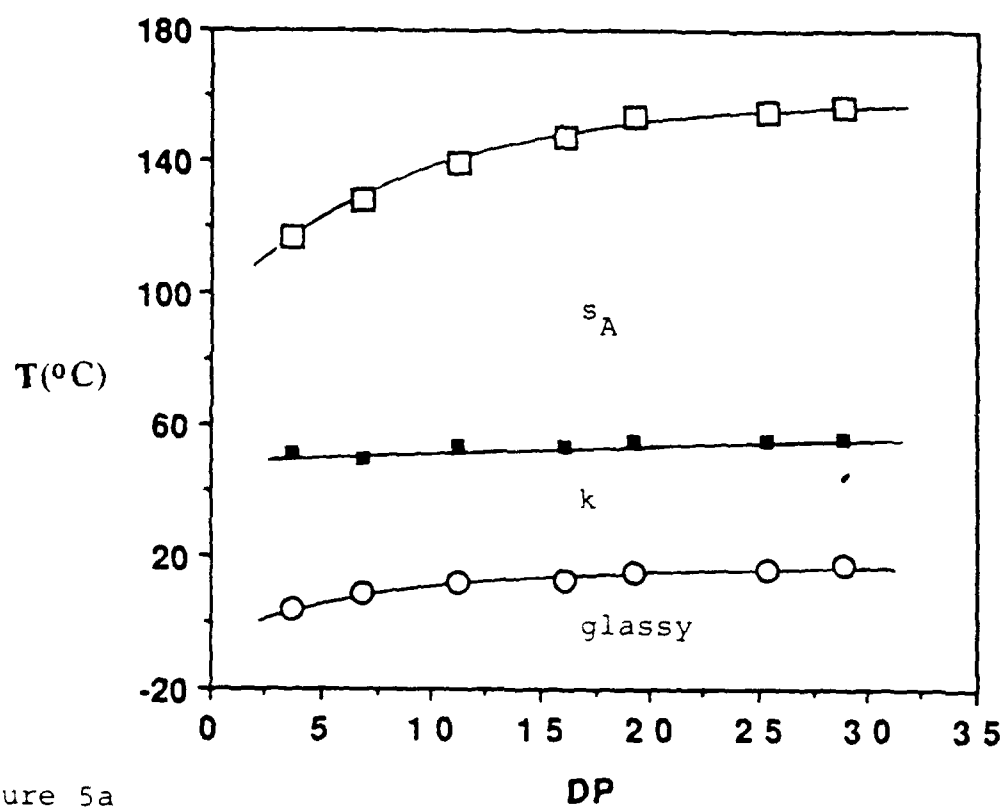


Figure 5a

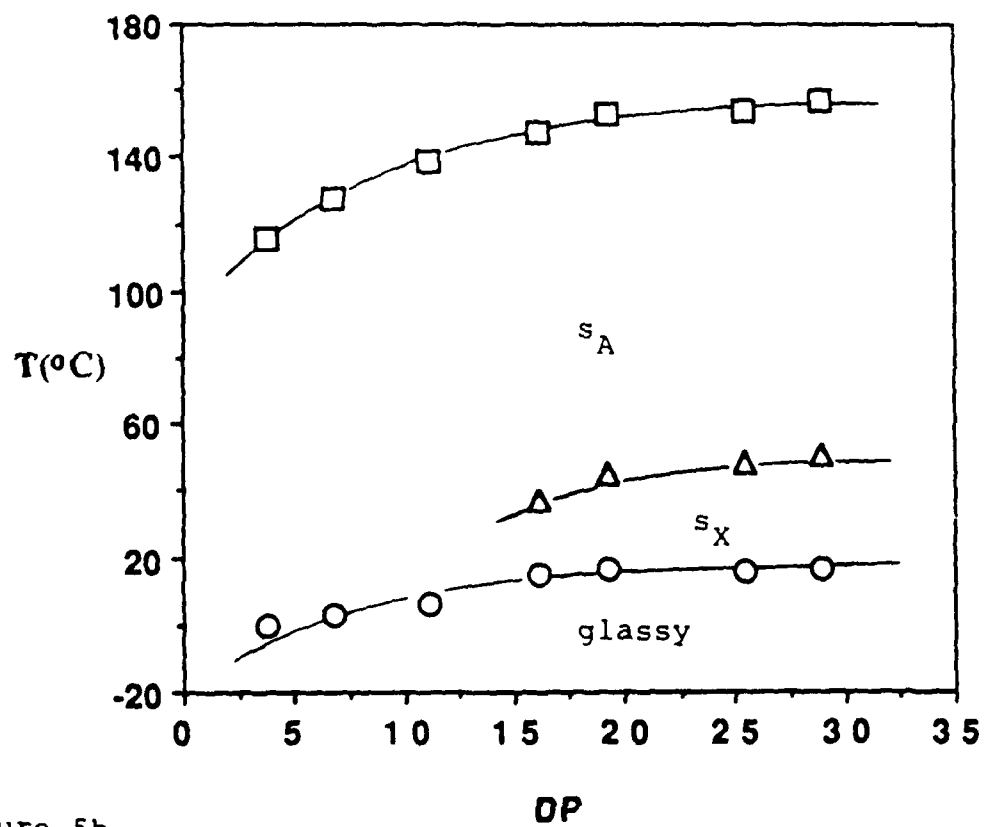


Figure 5b

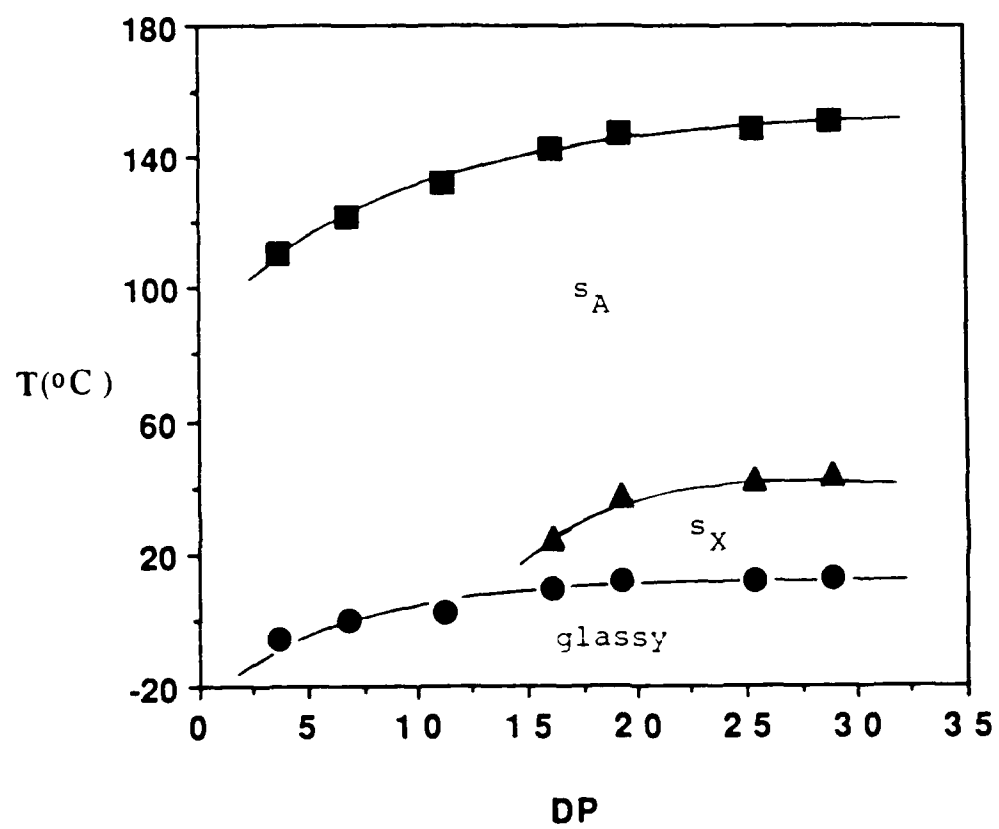


Figure 5c



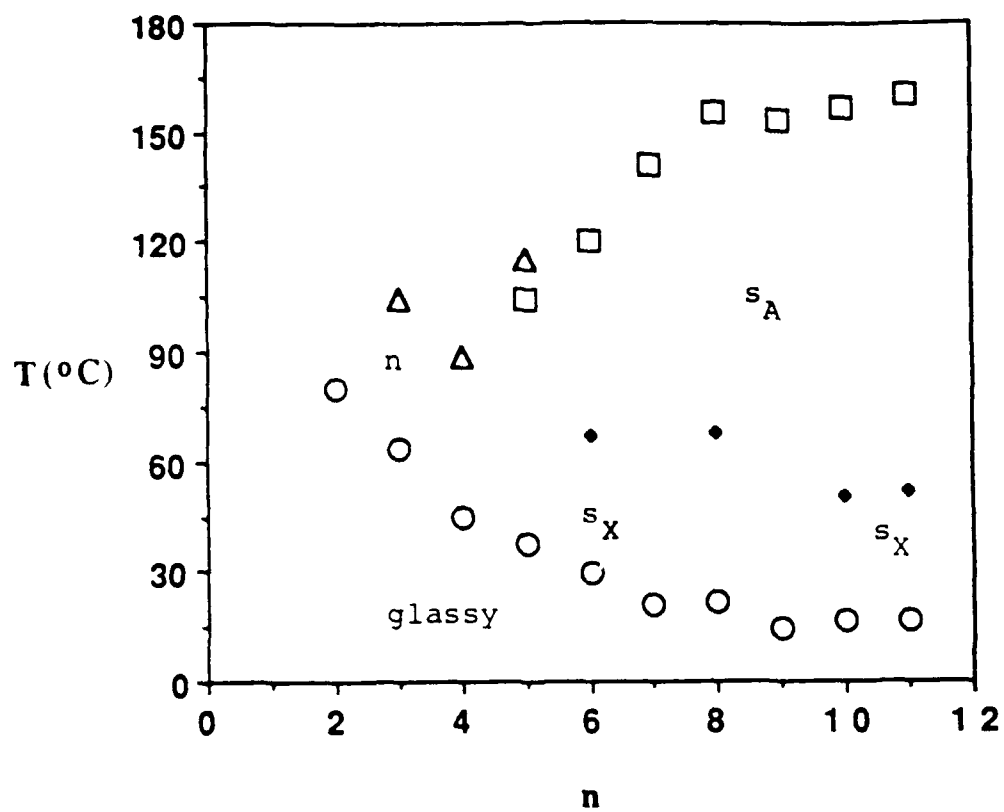


Figure 6a

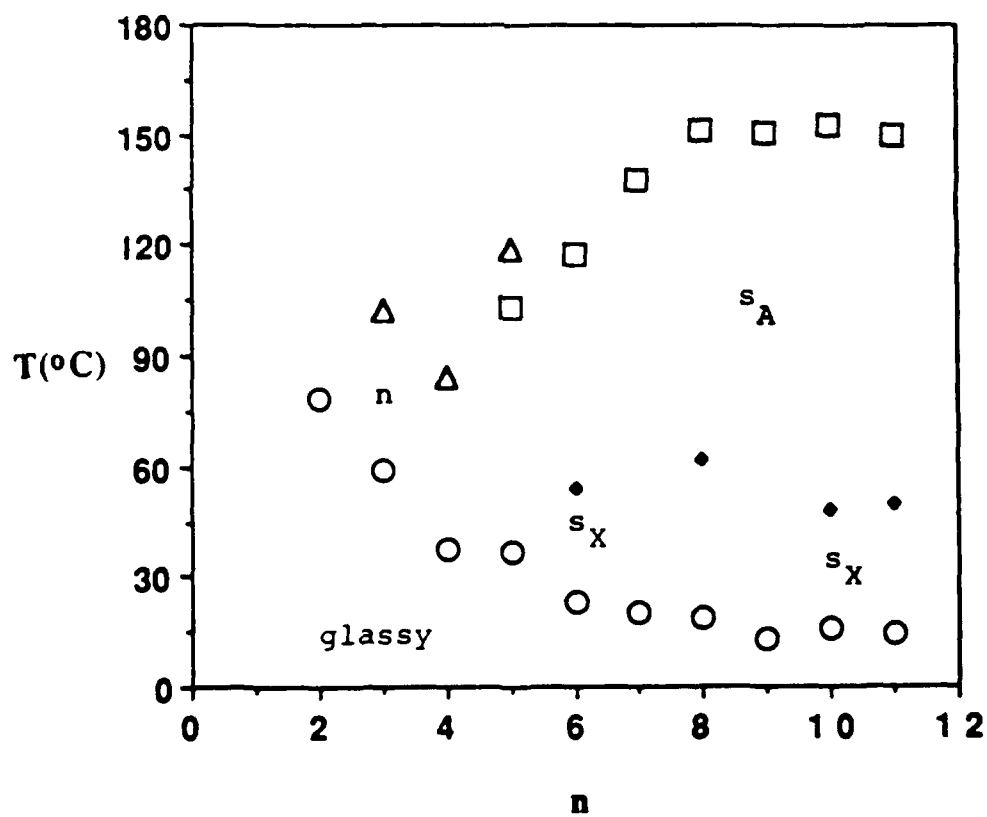


Figure 6b

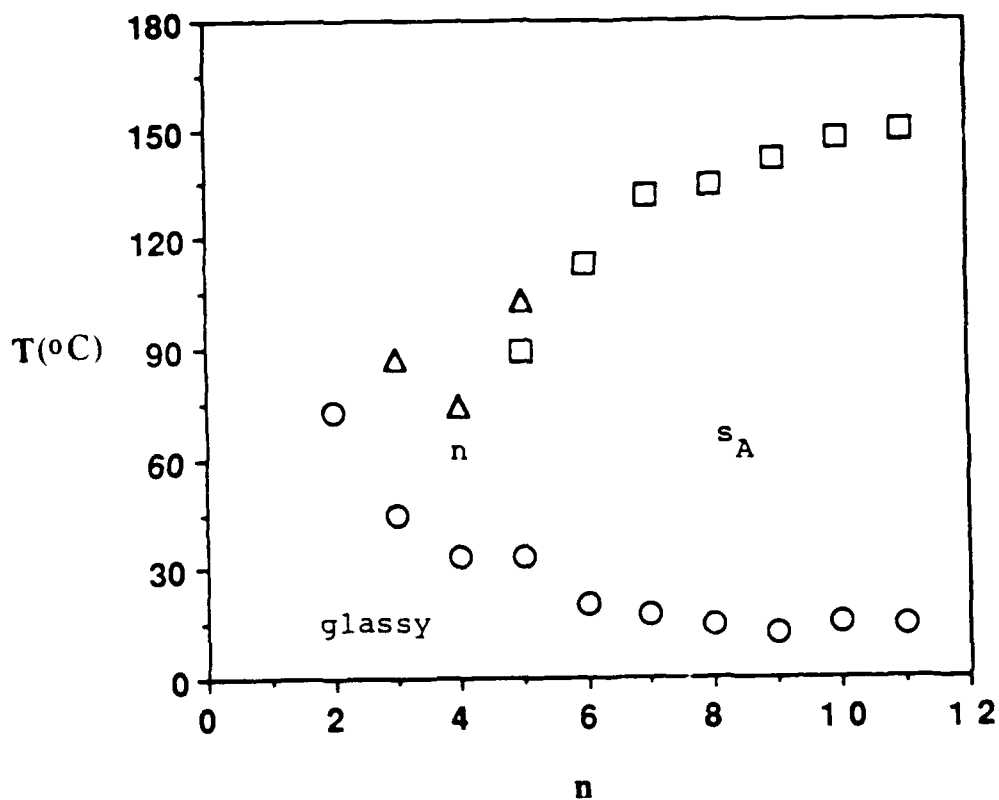


Figure 6c

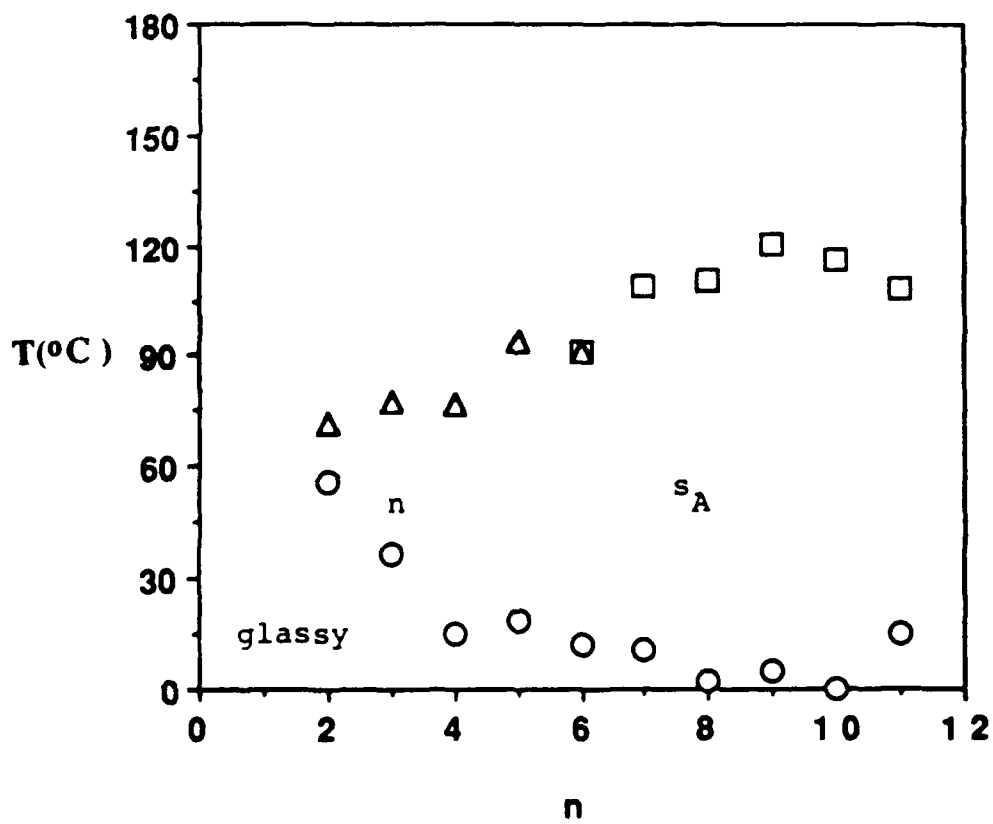


Figure 6d

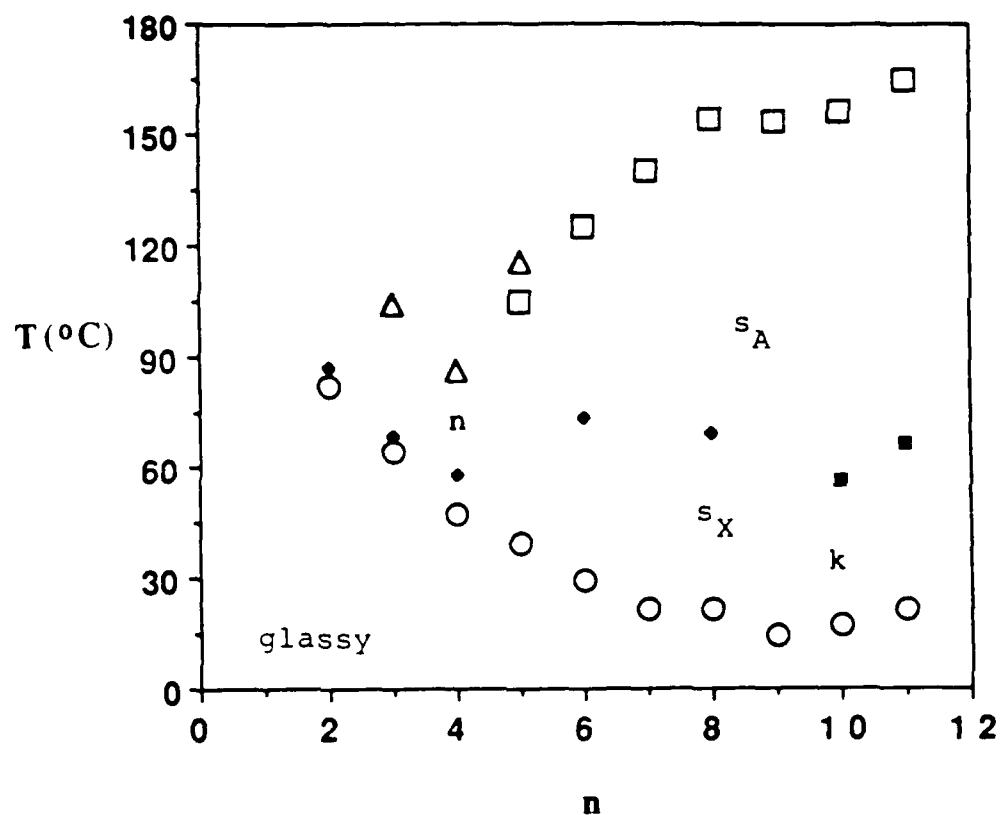


Figure 7a

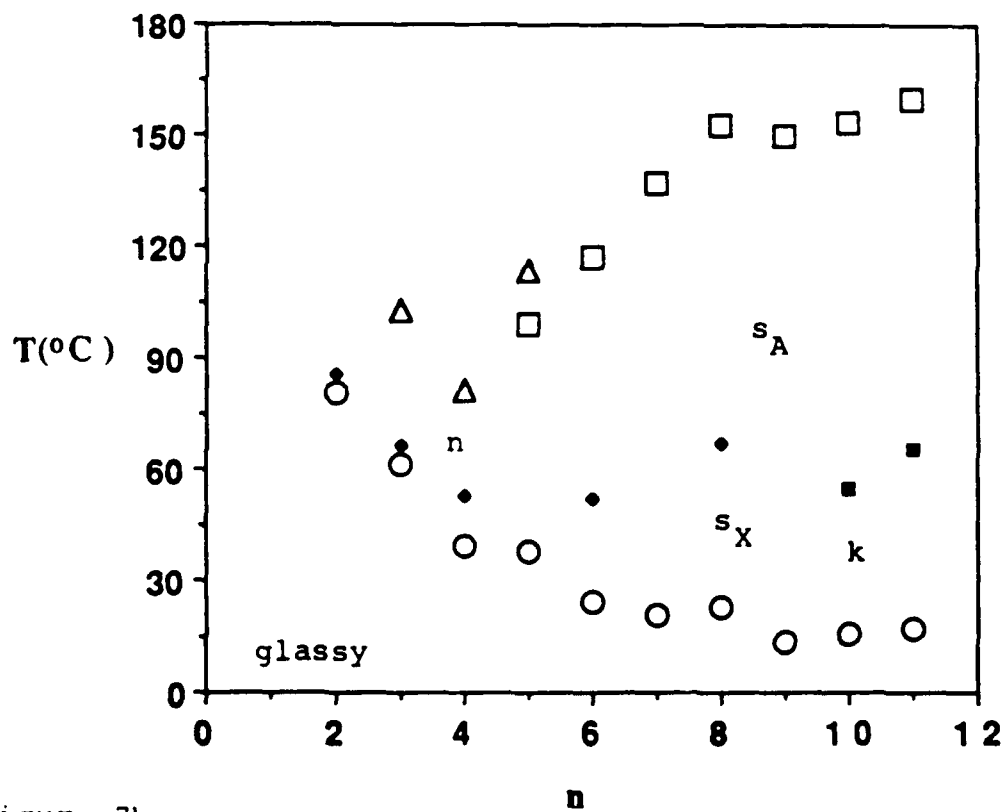


Figure 7b

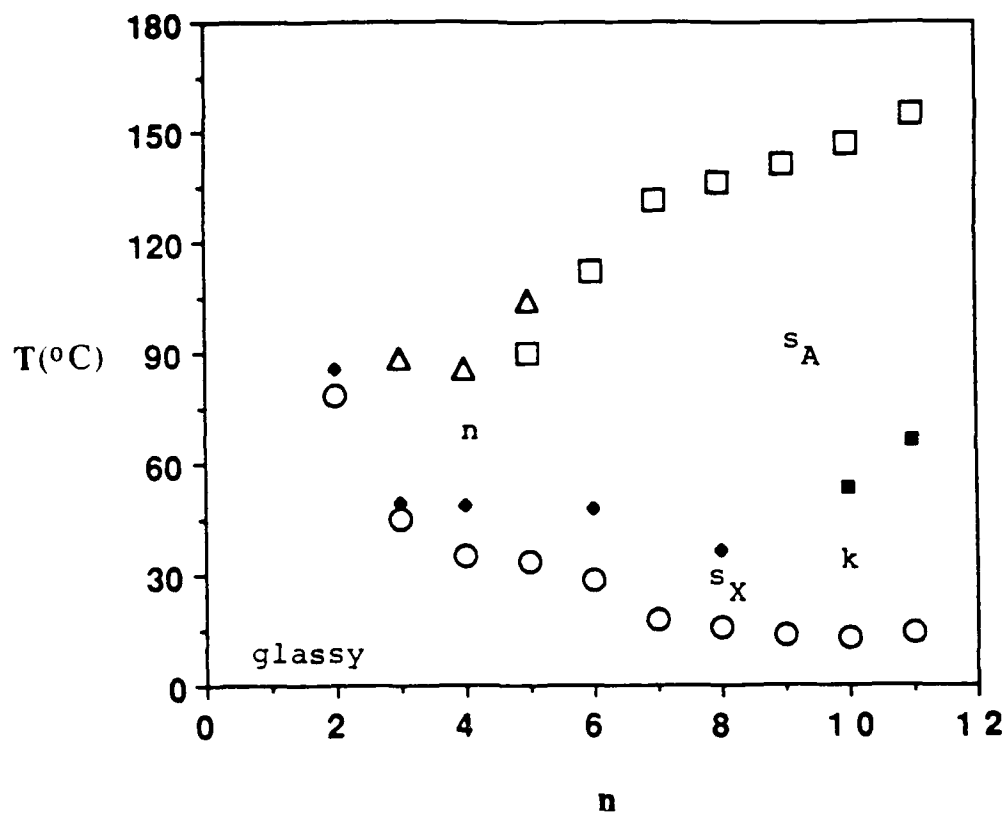


Figure 7c

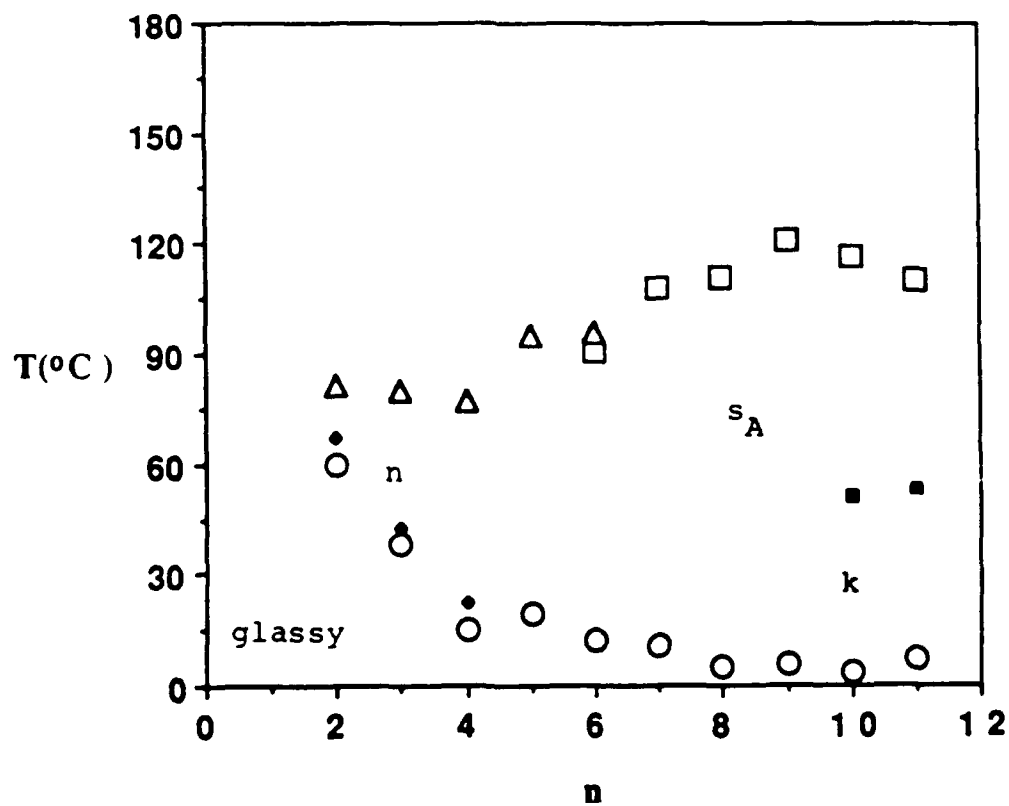


Figure 7d